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AUTOMATED ANALYSES FOR ENVIRONMENTAL POLLUTION CONTROL

L. J. Kamphake, et al

National Environmental Research Center
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ABSTRACT

Environmental monitoring and pollution control have become, in recent years, topics of increasing national and international interest. Analytical methodology has become a very important tool in our efforts to abate pollution. It is this technology which allows us to quantify the "state of the environment" which serves as a bench mark for measuring progress. We use this technology to measure process performance, achieve process control, distribute costs, express standards and enforce our pollution laws. Accurate, precise and reproducible analytical methods are a cornerstone of all pollution control activities. Improved automated analytical techniques which have these attributes and offer the advantages of economy and speed of execution are greatly needed.

Techniques and development of automated analysis for parameters requiring wet-chemical methods, utilizing the Technicon AutoAnalyzer are presented. Also, their application is discussed for the continuous monitoring of wastewaters and control of various treatment processes for nitrogen and phosphorus removal.

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L. J. Kamphake and R. T. Williams

L. J. Kamphake, Research Chemist, Waste Identification and Analysis Activities, Advanced Waste Treatment Research Laboratory, National Environmental Research Center, Environmental Protection Agency, Cincinnati, Ohio 45268.

R. T. Williams, Acting Chief, Waste Identification and Analysis Activities, Advanced Waste Treatment Research Laboratory, National Environmental Research Center, Environmental Protection Agency, Cincinnati, Ohio 45268.

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This decade of the '70's may one day be called the decade of the environment. Environment, pollution and ecology have become everyday words and the public is aware of the spoiling of the land, the fouling of the air and the many types of water pollution. Many individuals, civic groups and industries have joined the various levels of the Government in its attack on pollution.

In December of 1970, President Nixon established the U. S. Environmental Protection Agency and assigned to it responsibility for all operational and research efforts in the fields of air, solid waste, pesticides, radiation, noise pollution as well as the advanced waste water treatment research underway at the National Environmental Research Center in Cincinnati where the authors of this paper are conducting the work described herein.

Last August, Cincinnati was designated by the United States Environmental Protection Agency as one of the three National Environmental Research Centers, the other two being Corvallis, Oregon, and Research Triangle Park, North Carolina. The Cincinnati Center has a broad charter to

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deal with the total environment in research and monitoring programs, with special emphasis on environmental protection engineering. The construction contracts for a new $28 million multi-environmental sciences complex to be built near the University of Cincinnati campus is in process.

It is difficult to quantify the economic impact of pollution. The Environmental Protection Agency (EPA) of the U. S. Government, has for example, estimated that the cost of air pollution with regard to its effect on health, vegetation and property is more than $16 billion annually. The cost of water pollution damage is even harder to quantify. Qualitatively we can see the degradation of the quality of our lakes, rivers and ocean, reduced yields of fresh water and coastal fisheries, increased costs for treating water supplies for industrial agricultural and metropolitan needs and even losses in use of our water resources for recreational purposes.

Environmental monitoring and pollution control activities require accurate, precise and reproducible analytical techniques. The automation of such analytical procedures offers the potential to increase reproducibility by reducing the human error and also reducing the

time and expense of repetitive analyses. Automated sensors (1,2,6) with continuous readout for the measurement of the key parameters associated with pollution would be ideal.

Continuous sensors, for parameters such as temperature, dissolved oxygen, conductivity, pH and chloride are available (7). These sensors work on a physical-chemical property of the parameter that is related to an electronic signal. After a relationship between the parameter and an electronic signal is achieved, there is almost no limit to the degree of automation that can follow. The electronic technology is already available for applying the sensor's signal to continuous monitoring with subsequent telemetering and conversion of the signal to meaningful data through computerization. Our present objective is to obtain sensors that can be used continuously for parameters that are more meaningful to water pollution than those already mentioned. Sensors to measure the parameters that are indicative of the operational efficiency of removal treatment processes being applied to municipal and industrial waste are needed. However, such parameters as COD, total phosphorus, phenol, cyanides, ammonia, nitrite and nitrate, all require intermediate wet chemical reactions before they can be detected by spectrometric sensors and be relayed by

an electrical signal. The objective of this paper is to present the manner in which the Advanced Waste Treatment Research Laboratory has applied the AutoAnalyzer, in the laboratory, to individual samples, and in a waste treatment plant to continuous monitoring of an effluent.

The Technicon AutoAnalyzer* has been proven to be satisfactory for rapid, automated wet-chemical analysis on individual samples. Its use in water pollution laboratories is so widespread that Automated Standard Methods (11) for water pollution are published for some chemical parameters.

During the past ten years, the Waste Identification and Analysis Section has provided the analytical needs for research on new wastewater treatment processes on plant and pilot plant studies at the Advanced Waste Treatment Research Laboratory. Ability to handle a large number of analyses with good accuracy is essential because much of the data is used in mass balance calculations (12). The analytical laboratory is the "measuring stick" for the evaluation of each new treatment process. Samples may vary

* Technicon AutoAnalyzer is manufactured by Technicon Instrument Corporation, Tarrytown, New York. Mention of this product is for identification only and does not constitute endorsement by the Environmental Protection Agency of the U. S. Government.

in consistency from that of activated carbon of ion exchange column effluents to digester sludges. Automated laboratory methods were developed and used for the analysis of ammonia, nitrite, nitrate, ortho and total phosphorus, aluminum, ferrous and total iron, A B S, sulfate, and methanol.

The success of each analytical system is primarily dependent upon the manifold design. Effort is made to achieve the maximum rate of each chemical reaction by determining the optimum conditions of time, temperature, pH and reagent concentration. When this is obtained there is generally an increase in the sensitivity, thus requiring a smaller sample aliquot with less chance of interfering ions, a shorter flow stream through the system which will produce a faster response and wash out, and smoother, steadier plateaus. The laboratory AutoAnalyzers operate at a rate of 20 to 30 determinations per hour with no washes between samples. A control blank and standard placed after every ten samples serves a dual purpose of quality control and ease of identification of samples on the strip chart recorder. All the systems can operate unattended and be turned off after working hours by electric timers, resulting in the completion of two hundred more analyses.

The continuous flow-system of the AutoAnalyzer has a unique advantage when determining the rate of chemical reactions. This system permits the application of a controlled gradient concentration technique which is a rapid way of determining the optimum concentration of reagent for a reaction and in determining the limits of interfering agents in a method. Gradient concentration (IC) can be defined as a controlled rate of increase (or decrease) of the concentration of a specific material in a constant flowing stream. When applied to the AutoAnalyzer for investigating possible interferences the delay time, or the time between sampling and recorder response, must first be determined. This can be accomplished by measuring time of travel of a densely colored solution through the system. A high concentration (100, 1000, or 10,000 mg/l) of a suspected interference or a reagent is pumped into a known volume of distilled water, mixed instantaneously, and simultaneously pumped out of the dilution reservoir into the sample stream, as shown in Figure 1. The concentration of the stock solution (c) in the sample stream (C_t) can be calculated at any time (t) when the pump into (R_i = influent rate) the gratient reservoir (V) is the same as the pump rate out (R_e = effluent rate) of the reservoir by the equation

$$C_t = c\left(1 - E^{-Rt/V}\right)\frac{S}{R}$$

where E, the Napierian base, equal 2.7183 and S is the flow volume of the sample or standard.

A more complex calculation results when the flow rate into the reservoir is not the same as the flow rate out of the reservoir. Such may be needed in determining the optimum concentration of a reagent for chemical reaction, when the rate of addition and the solubility of stock solution are limited. When R_o does not equal R_i the following equation is used for calculation:

$$C_t = c\left[1 - \left(1 + \frac{\Delta Rt}{V}\right)^{-R_i/\Delta R}\right]\frac{S}{R_o}$$

where ΔR is the difference between R_o and R_i.

The number of calculations can be reduced by plotting a series of curves of concentrations vs. time or simplified by programming into laboratory computers. Concentrations in the reaction stream can be related to the recorder tracing by adding the delay time to the initial starting time of gradient concentration.

In a laboratory system where a wider range of sensitivity might be needed to analyze various types of samples, two or three sample or diluent tubes is an advantage. For example, a manifold can be prepared for the analysis of

phosphorus, utilizing three sample-diluent tubes that will produce a ten-fold dilution of the smallest sample tube and a range of analysis from .010 to 20.0 mg/l phosphorus when either 8 or 50 mm colorimeter cells are used. This can be done without changing the basic chemistry within the system.

To some chemists, the numerous variables associated with the AutoAnalyzer that produce changes in the chemistries of the analytical method cause much confusion, while others utilize this versatility of the AutoAnalyzer to obtain a better understanding of the chemistry involved.

There is a limit to the concentration of many ions that can cause either a positive or negative interference in every colorimetric reaction. The hydrogen ion or pH is undoubtedly the most significant of these. The effect of pH on the nitrite color reaction, which is also used in many nitrate methods, is shown in Figure 2. Between pH 1 and 2 there is no change in the completeness of the color reaction. However, as the pH increases above pH 2, there is a progressive decrease in sensitivity.

The same effect can be caused by high concentrations of alkalinity or acidity in the sample, as shown in Figure 3. Samples can be analyzed, with this particular manifold, containing up to 800 mg/l of alkalinity or acidity. Higher

concentrations of alkalinity will produce a negative interference. Similar data should be obtained for all suspected interferences for each manifold.

Continuous Monitors

One of the most detrimental results of water pollution is the eutrophication of lakes and streams due to overstimulation of plant life. This excess plant growth is caused by excess nutrients such as carbon, nitrogen and phosphorus. Much of the nitrogen, in the form of ammonia, nitrite and nitrate, along with organic carbon and phosphorus are present in the lakes and streams as a result of pollution. Unfortunately to date, much of the wastewater that reaches our streams and lakes has had little or no treatment which effectively removes these nutrients.

Combined biological-chemical treatment systems for the removal of phosphorus and nitrogen are now available (12) for treatment of wastewaters. In order to operate these treatment processes, which require the addition of lime, alum or methanol, at the lowest cost and highest efficiency possible, continuous monitoring for phosphorus and nitrogen is a necessity. In a recent analysis, we found that continuous monitoring of the influent phosphorus concentration to control the chemical addition rate could save $40,000 per year in a 10 MGD plant.

Several criteria or objectives have been established for using the AutoAnalyzer for continuous monitoring: 1. Capability for continuous operation for one week with a minimum amount of attention (less than four hours per week) and with at least a $\pm$ 5% accuracy at the 50% (.30 absorbance) absorption concentration; 2. the reagents must be stable for a week; 3. the reagent consumption must be low (less than 4 liters per week); 4. that the baseline must be stable. It is also desirable that the colorimetric chemistry obey Beer's Law for easy and rapid calculations and the minimum distance of flow stream in the system be obtained for a fast response and equilibrium of the system.

A manifold that was designed for the continuous monitoring of total nitrite and nitrate nitrogen for an experimental pilot plant study (4) is shown in Figure 4. The purpose of the pilot plant study was to determine the methanol-nitrogen ratios necessary for biological denitrification of nitrified effluent by passage through a column filled with various sized inert media. The optimum conditions and reagent concentrations were incorporated in the new manifold for a one RPM proportional pump in place of the usual four RPM pump, as published by Kamphake, et al. (9). The procedure is based on the reduction of nitrate to nitrite by hydrazene sulfate with analysis of the resultant nitrite.

Considerable baseline drift occurred when the system was operated in the atmosphere of the sewage treatment plant due to development of color in the nitrite diazotization-coupling reagent. In order to determine the cause of this color formation, small quantities of the reagent were exposed to various conditions of temperature, light, and air. The absorbency of each was read daily over a period of a week. As shown in Table 1, the greatest amount developed when the reagent was exposed to air. An airtrap, containing a small amount of the reagent, was placed on the stock reagent container. This prevented the absorption of nitrogen oxides in the atmosphere from contaminating the stock reagent and thus prevented the baseline drift.

The degree of sensitivity of the system to detect a change in the concentration of the sample stream is partially dependent upon the response time and the washout time. This is of value in determining the minimum sampling time. Response time is defined as the number of minutes required for a system to reach equilibrium when changing from distilled water to a standard (or sample) which produces 80% absorption. Figure 5 shows the time required to reach equilibrium for four different concentrations. Ten minutes of sampling is required for this system to reach a

maximum of .75 absorbance (80% absorption) for a 20 mg/l nitrate standard.

Washout time is also of importance in checking the baseline. It is defined as the minimum time required for a system to reach equilibrium at the baseline when changing from a high standard (80% absorption) to distilled water. Figure 6 shows the time required to reach equilibrium at the baseline when sampling from four different standards. Ten minutes of sampling distilled water is required for this system to return to the baseline after sampling a 20 mg/l standard. Since the minimal response and washout time is ten minutes, and allowing five minutes for establishing a sample plateau, a total of fifteen minutes is required for sampling to detect the maximum change in concentration of the sample stream.

The response rate and washout rate is primarily dependent upon the hydraulics of the system. This continuous nitrate manifold was used with a 1 RPM proportional pump instead of the usual 4 RPM pump, and had a rather low flow volume per minute (1.85 ml per minute) and a rather long distance of travel (> 50 ft.). An increase in the flow rate and a shorter distance of travel would produce a faster response and washout rate and decrease the delay time

between sampling and recorder response. These ideas were incorporated later in the design of the continuous phosphorus manifold. However, this continuous nitrate-nitrogen manifold was feasible and valuable in the pilot plant study for determining the minimal amounts of methanol needed for denitrification (4).

An automated sampling system was designed for multiple sample streams and standards. As shown in Figure 7, it consists of a multi-channel electric timer, solenoid-operated values and a series of flow lines. The denitrification study was completed before this was evaluated.

Phosphorus Monitor

The need for an automatic sensor to aid in feeding chemicals into a coagulation for phosphorus removal system (3) has long since been recognized. Wet-chemical methods of analysis are presently the only practical means of measuring phosphorus. The most universal wet-chemical method is based on the formation of phosphomolybdic acid which is a yellow color at high concentration of phosphorus. The sensitivity is greatly increased by reducing the phosphomolybdic acid to a blue complex. Stannous chloride is the established reductant in manual procedures. When this procedure is adapted to the AutoAnalyzer difficulty is usually caused by

precipitation and a buildup of a coating of the basic tin salt within the colorimeter cell, which cause baseline drift. Other reductants, such as ascorbic acid and amino-naphthol sulfonic acid have overcome the coating effect but are not sufficiently stable for a continuous monitoring system. Hydrazine sulfate is known to be a very stable reductant in an acidic solution, and is also used as a reductant for phosphomolybdic acid.

A manifold was designed, as shown in Figure 8, utilizing hydrazine sulfate as the reductant, for continuous monitoring of ortho phosphorus in the effluent from 1.6 MGD sewage treatment plant. The objective of a study being conducted at the sewage treatment plant in Richardson, Texas was to control the amount of coagulant needed for phosphorus removal in order to maintain a final effluent with less than 0.5 mg/l phosphorus (13). The new phosphorus manifold fulfilled all the criteria previously mentioned for a continuous monitoring wet-chemical sensor. A baseline was maintained with less than .020 absorbance (4% absorption) drift for a week when sampling either distilled water, or after sampling a phosphorus standard or a spiked effluent sample which produced approximately .92 absorbance (88% absorption). The analyzer was inoperative

for only five days out of the 90 days of continuous monitoring. Daily standardization showed no significant change in sensitivity. After six months of operation it was noticed that the suspended solids in the plant's final effluent were sufficiently low that the continuous paper filter could be removed without any adverse effect. No interference was caused by 1.0 mg/l of free chlorine. However, with 1.5 mg/l of free chlorine a decrease in sensitivity was observed.

Investigations of all the operating conditions, reagent concentrations, and other possible interferences are being conducted and will be published in the future (5).

Conclusion

The present status of our continuous wet-chemical monitors is similar to where our automated laboratory methods were ten years ago. Increased knowledge of conditions for optimum chemical reactions, stability of reagents, and elimination of interferences have added greatly to the development of continuous monitors for nitrate-nitrite nitrogen and total ortho-phosphorus. With these continuous monitors it is possible to monitor the effluent from waste treatment plants and control the treatment process more accurately and efficiently than ever before.

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Listing of 8 Figures and 1 Table as follows:

Figure 1 Controlled Gradient Concentration

Figure 2 Effect of pH on Nitrite Color Reaction

Figure 3 Interference of Alkalinity on Nitrite Color Reaction

Figure 4 Continuous Nitrite Plus Nitrate Manifold

Table 1 Stability of NO_2 Color Reagent

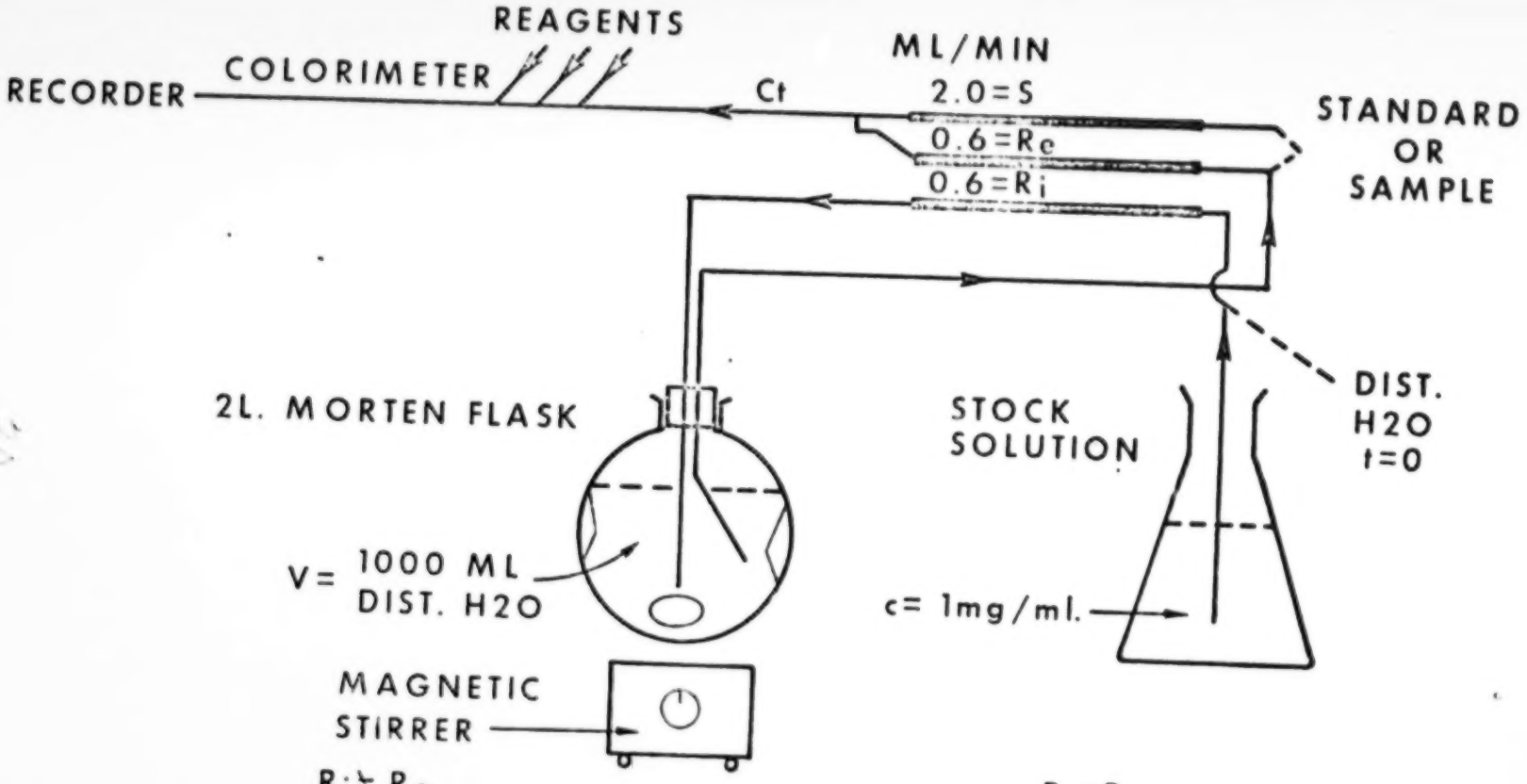
Figure 5 Nitrate Response Rate Continuous Manifold

Figure 6 Nitrate Washout Rate

Figure 7 Automatic Sampling System

Figure 8 Continuous Phosphorus Manifold

CONTROLLED GRADIENT CONCENTRATION



$R_i \neq R_e$

$$C_t = c\left[1-\left(1+\frac{\Delta Rt}{V}\right)^{-Ri/\Delta R}\right]\frac{S}{Re}$$

$R_i = R_e$

$$C_t = c(1-E^{-Rt/V})\frac{S}{R}$$

t=TIME (MIN.)

E=NAPIERIAN BASE = 2.7183

Figure 1

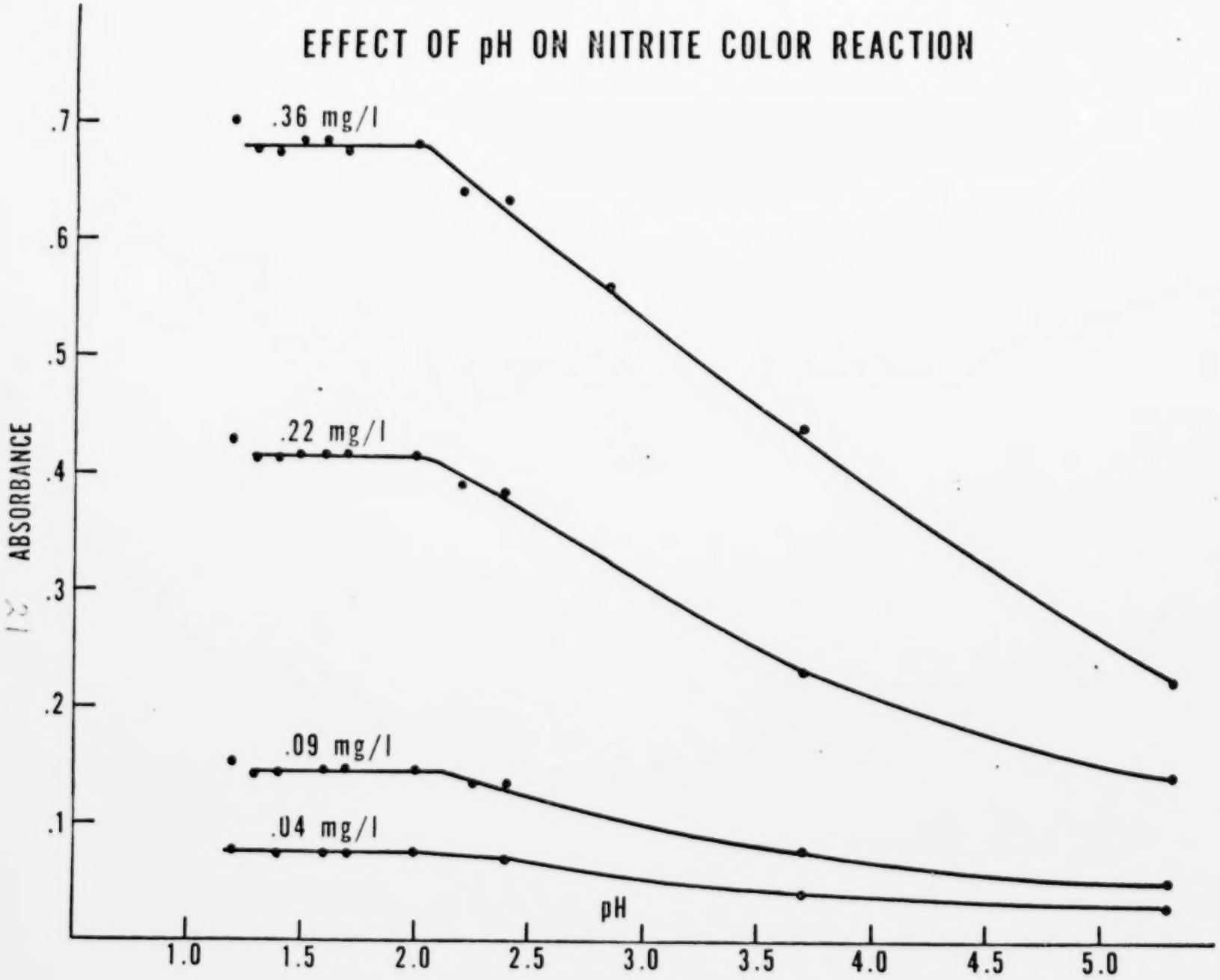

EFFECT OF pH ON NITRITE COLOR REACTION
.36 mg/l
.22 mg/l
.09 mg/l
.04 mg/l
ABSORBANCE
.7
.6
.5
.4
.3
.2
.1
pH
1.0
1.5
2.0
2.5
3.0
3.5
4.0
4.5
5.0

Figure 2

INTERFERENCE OF ALKALINITY ON NITRITE COLOR REACTION

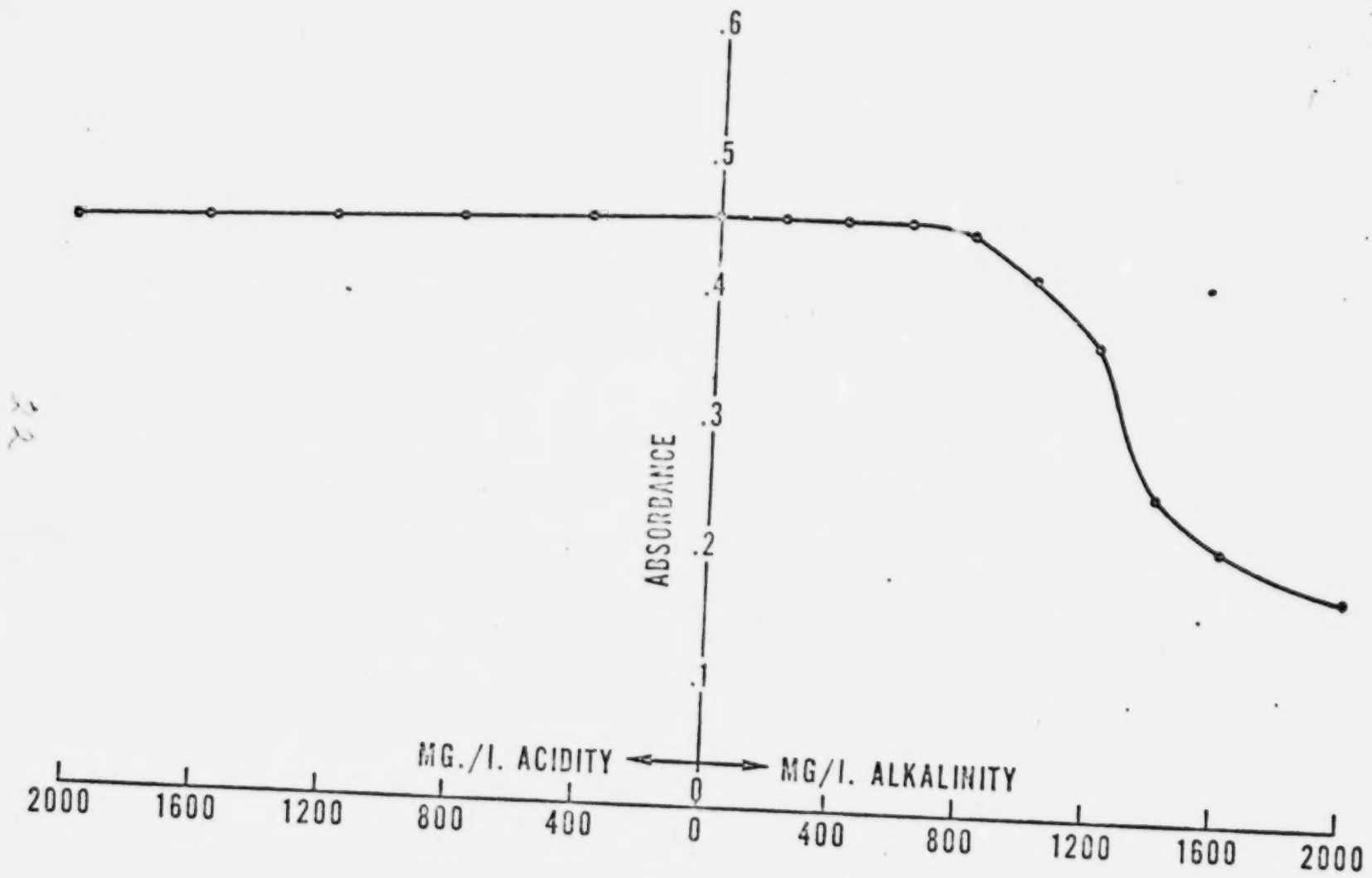
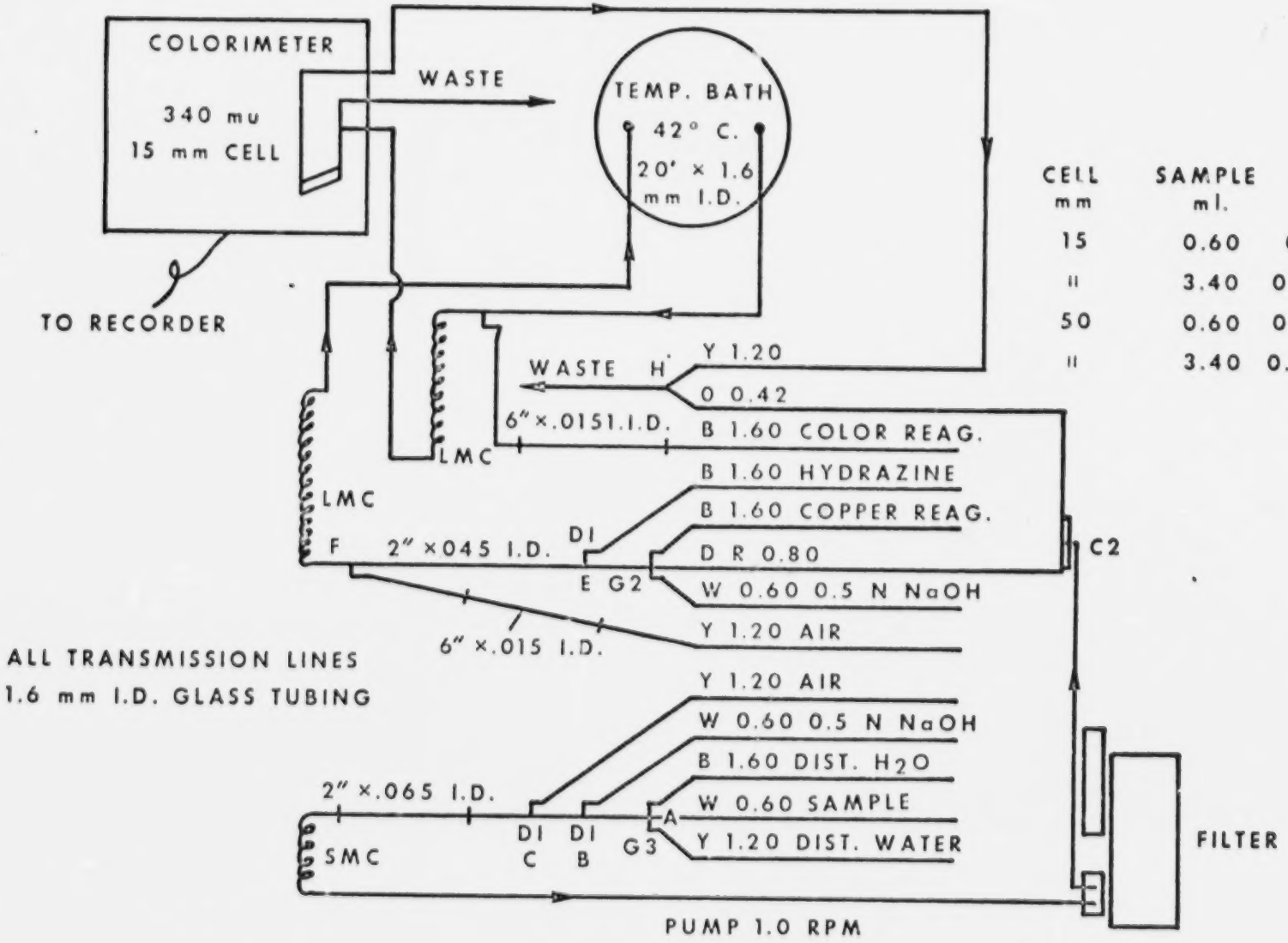


Figure 3

CONTINUOUS NITRITE PLUS NITRATE MANIFOLD

L.J. KAMPHAKE FEB. 1969



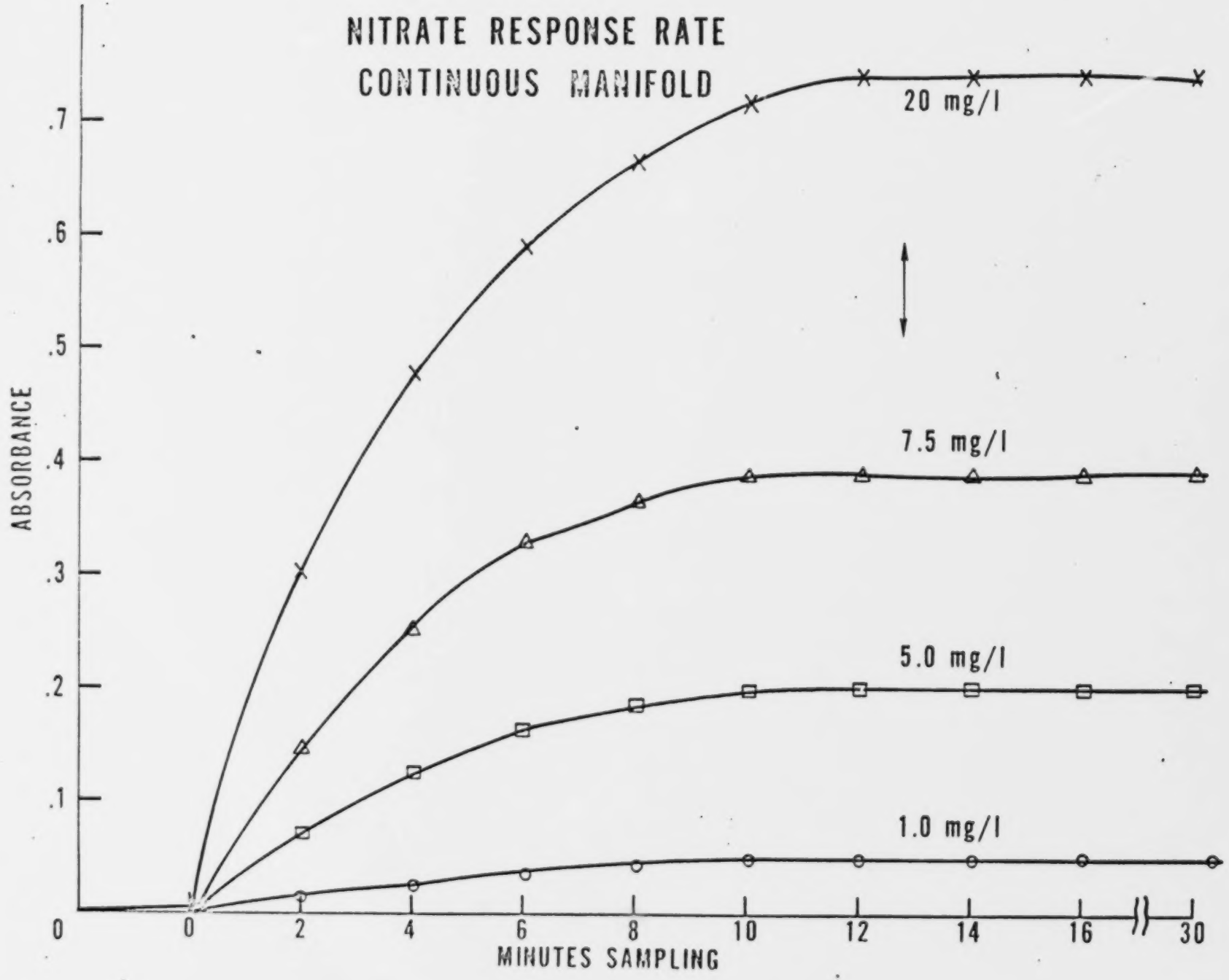
CELL mm	SAMPLE ml.	RANGE mg/l.
15	0.60	0.1 TO 30.
"	3.40	0.05 5.
50	0.60	0.03 10.
"	3.40	0.015 1.5

Figure 4

STABILITY OF NO_2 COLOR REAGENT

CONDITION	ABSORBANCE DAYS				
	0	1	2	5	7
CLOSE-DARK 5°	.015	.020	.022	.032	.032
CLOSE-DARK 25°	.015	.020	.030	.038	.045
CLOSE-LIGHT 5°	.015	.020	.020	.025	.022
CLOSE-LIGHT 25°	.015	.026	.020	.030	.045
OPEN-LIGHT 25°	.015	.164	.355	.785	1.27

Table 1


NITRATE RESPONSE RATE
CONTINUOUS MANIFOLD
20 mg/l
7.5 mg/l
5.0 mg/l
1.0 mg/l
ABSORBANCE
.7
.6
.5
.4
.3
.2
.1
0
0
2
4
6
8
10
12
14
16
30
MINUTES SAMPLING

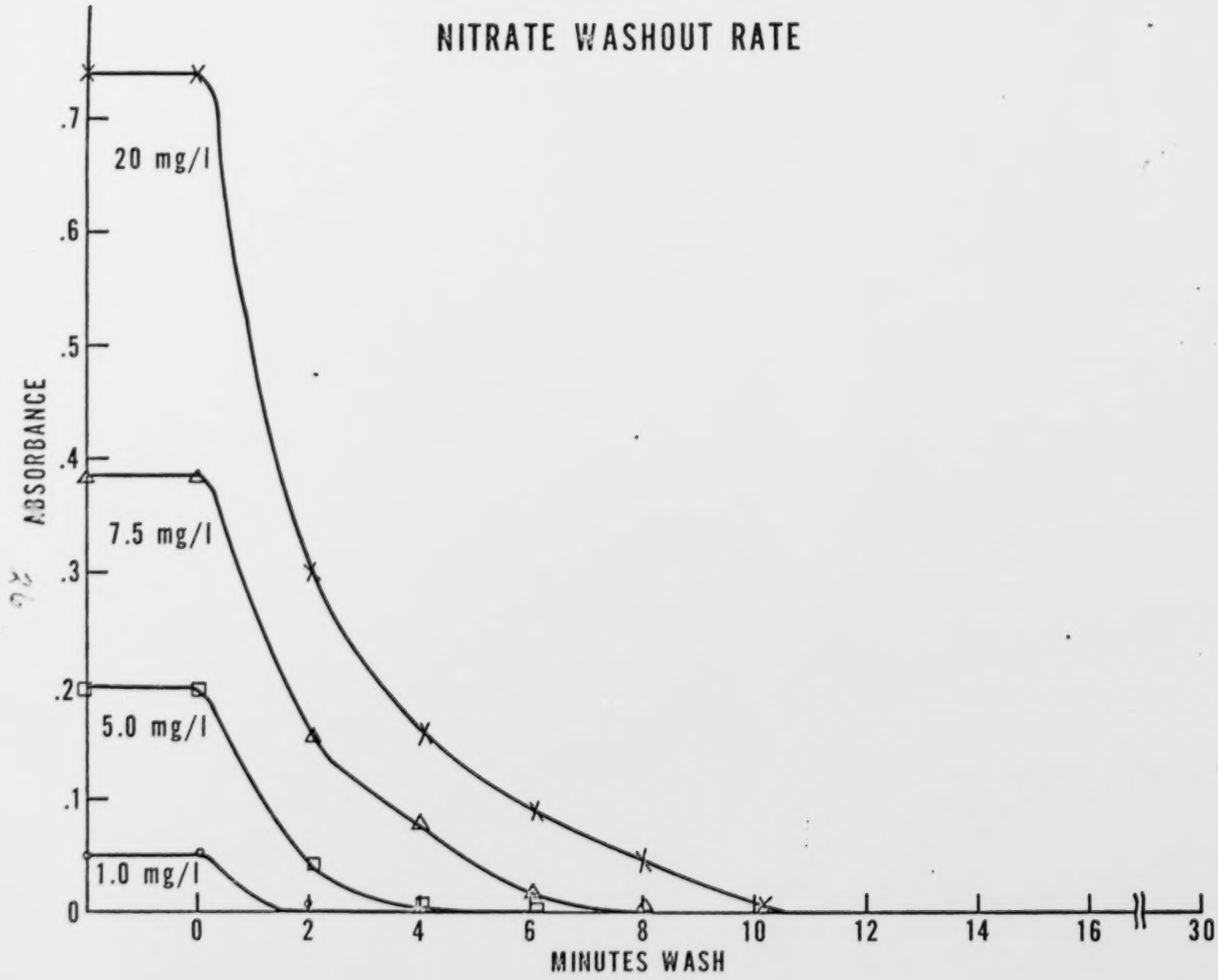

NITRATE WASHOUT RATE
ABSORBANCE
.7
.6
.5
.4
.3
.2
.1
0
20 mg/l
7.5 mg/l
5.0 mg/l
1.0 mg/l
0
2
4
6
8
10
12
14
16
30
MINUTES WASH

Figure 6

AUTOMATIC SAMPLING SYSTEM

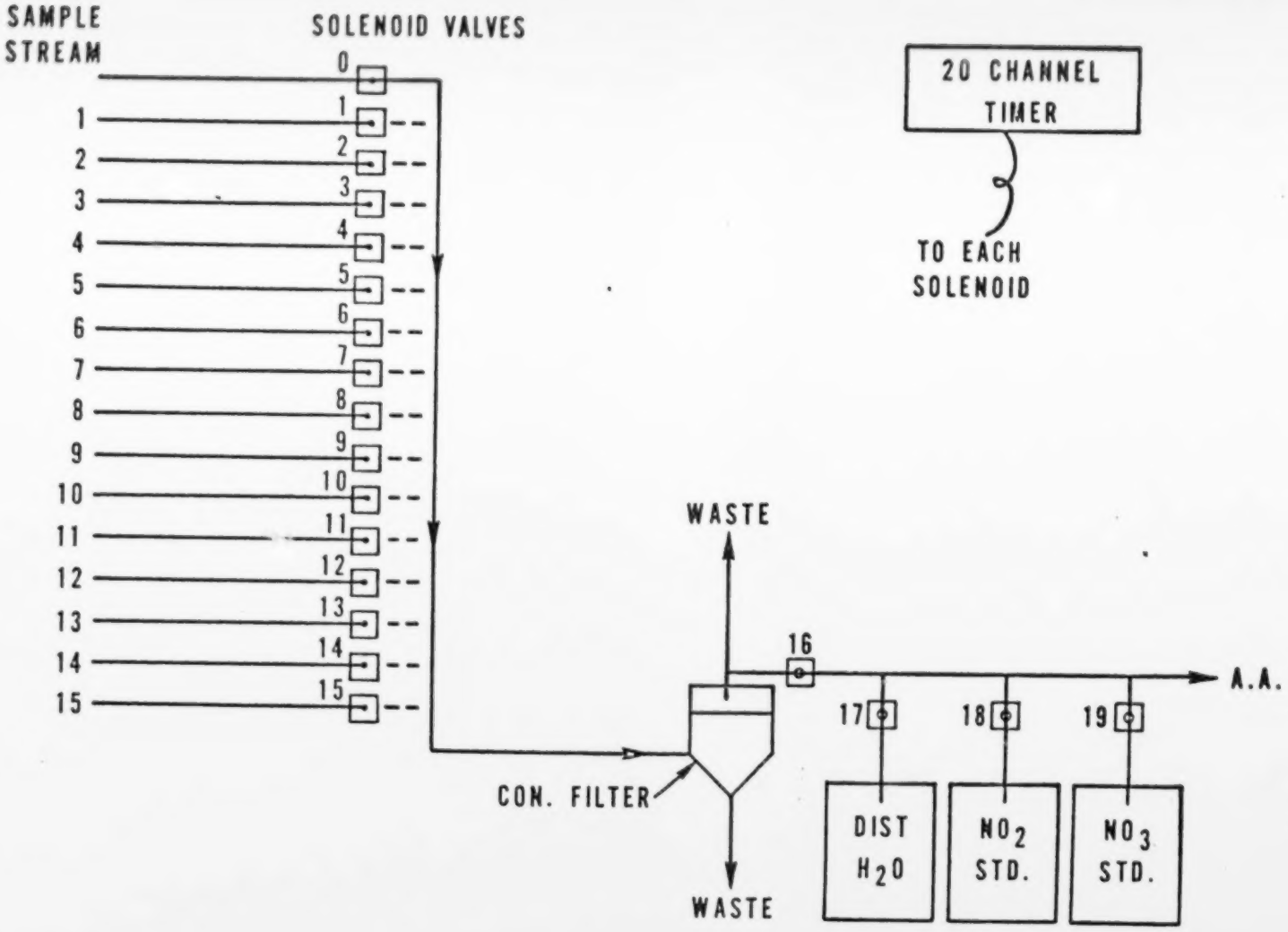


Figure 7

CONTINUOUS PHOSPHORUS MANIFOLD

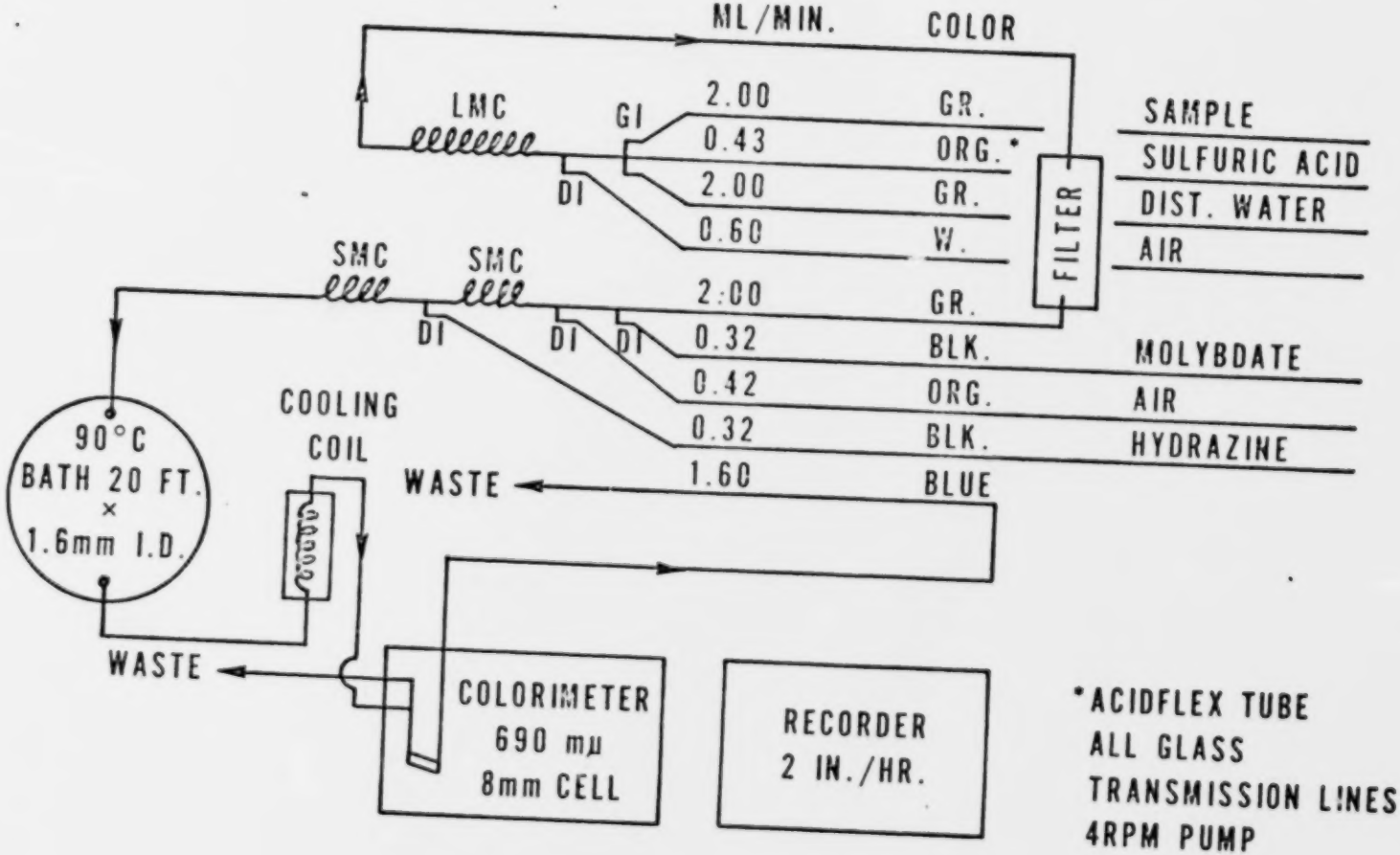


Figure 8